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Reduction of Np(VI) with Carbohydrazide in a Perchloric Acid Solution

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Abstract—The stoichiometry of the reaction of Np(VI) with carbohydrazide $(NH_2NH)_2CO$ in a 0.02 M $HClO_4$ solution was studied by spectrophotometry. With Np(VI) taken in excess, 1 mol of carbohydrazide reduces 5 mol of Np(VI) to Np(V). In 0.1–2.0 M $HClO_4$ solutions (the ionic strength of 2.0 was supported by adding $LiClO_4$) containing 3–100 mM $(NH_2NH)_2CO$, Np(VI) at a concentration of 1 mM at 20–45°C is consumed in accordance with a first-order rate law until less than 0.2 mM Np(VI) remains. Then the reaction decelerates. The reaction is first-order with respect to carbohydrazide and has the order of –1.45 with respect to H^+ ions. The activated complex is formed with the loss of 1 and 2 H^+ ions. The activation energy is 86 ± 5 kJ mol^{-1}.

Keywords: neptunium(VI), carbohydrazide, stoichiometry, perchloric acid, kinetics

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The extraction reprocessing of high-burn-up spent nuclear fuel based on uranium dioxide and on uranium nitride (for fast reactors) requires that the reagents used for reducing Pu(IV, VI), Np(VI), and Tc(VII) should form ultimately the minimal amount of mineral salts. Carbohydrazide $(NH_2NH)_2CO$ was suggested as one of such reagents [1]. It should be borne in mind, however, that carbohydrazide forms explosive compounds with some metal ions. For example, the carbohydrazide complex of iron(II) perchlorate exhibits properties of a high explosive [2]. Nevertheless, proper organization of the process allows accidents to be avoided. Therefore, it is quite justified to study reactions of actinides(VI, V, IV) and Tc(VII) with carbohydrazide. Volk et al. [1] studied the reaction of Np(VI) and Np(V) with carbohydrazide in HNO_3 solutions. They noted high rate of the Np(VI) reduction to Np(V) at room temperature. However, the kinetics of this reaction was not studied in detail.

In this work, we studied the stoichiometry and kinetics of the reaction of Np(VI) with carbohydrazide in $HClO_4$ solutions and outlined the process mechanism.

EXPERIMENTAL

The procedures for purifying ^{237}Np, preparing a stock solution of $NpO_2(ClO_4)_2$ in 0.02 M $HClO_4$, determining the Np concentration, and monitoring the valence forms were similar to those used previously [3]. The stock aqueous solution of carbohydrazide was prepared from a weighed portion of the compound (Acros Organics, the United States) containing no less than 97% main substance.

Perchloric acid and lithium perchlorate were of chemically pure grade; lithium perchlorate was additionally purified by recrystallization from water, followed by drying in air at 190°C. The stock and working solutions were prepared using double-distilled water. The $HClO_4$ concentration was determined by titration with a standard NaOH solution. The $LiClO_4$ solution was prepared from a weighed portion of the anhydrous recrystallized compound.

The experiment procedure was as follows. When studying the reaction stoichiometry, a temperature-controlled quartz cell (l = 1 cm) was charged with approximately 3 mL of an Np(VI) solution in 0.02 M $HClO_4$, the absorption spectrum in the range 950–990 nm was recorded with a Shimadzu PC 3100 (Japan) or SF-46 (Leningrad Optical and Mechanical Association, Russia) spectrophotometer, an $(NH_2NH)_2CO$ aliquot was added, and the absorption at a wavelength of 980.8 nm, corresponding to the main absorption band of Np(V), was measured at regular intervals. When studying the reaction kinetics, the cell was charged with a solution containing $HClO_4$, $LiClO_4$, and

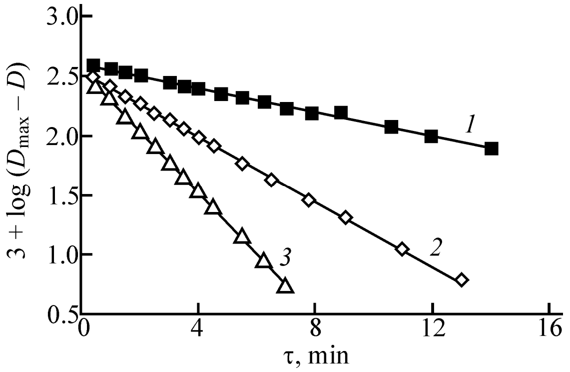

Fig. 1. Linearization of the kinetic curves of the Np(VI) reduction with carbohydrazide. [$HClO_4$] = 2 M, [Np(VI)] = 1 mM, T = 30°C, l = 1 cm; [$(NH_2NH)_2CO$], mM: (*1*) 20, (*2*) 50, and (*3*) 100.

$(NH_2NH)_2CO$ and was kept for 10–15 min at the preset temperature. After introducing an aliquot of the stock solution of Np(VI), the Np(V) accumulation was monitored. Each experiment was performed no less than in triplicate.

RESULTS AND DISCUSSION

The reaction stoichiometry was studied at 25–28°C. The Np(V) accumulation was observed in a 0.02 M $HClO_4$ solution containing 2 mM Np(VI) after adding $(NH_2NH)_2CO$ to a concentration of 0.2 mM. From the initial rate, we calculated the bimolecular rate constant and estimated the time of the 99.9% reaction completion. It should be equal to 10–11 min. Actually the optical density ceased to increase in 16 min. In the subsequent 3 h, the optical density increased by only 0.010. The Np(V) concentration was calculated using the molar extinction coefficient of Np(V), equal to 410 L mol^{-1} cm^{-1} [4]. In three experiments, we obtained $\Delta[Np(VI)]/\Delta[(NH_2NH)_2CO] = 5$.

Hydrazine exists in acid solutions in the cationic form. Presumably, carbohydrazide also takes up one or two protons in an $HClO_4$ solution. Therefore, the following reactions occur between Np(VI) and carbohydrazide:

$$NpO_2^{2+} + H_n(NH_2NH)_2CO^{n+} \rightarrow NpO_2^{+} + H^{+} + R_1, \quad (1)$$

$$NpO_2^{2+} + R_1 \rightarrow NpO_2^{+} + R_2, \quad (2)$$

$$NpO_2^{2+} + R_2 \rightarrow NpO_2^{+} + R_3, \quad (3)$$

$$NpO_2^{2+} + R_3 \rightarrow NpO_2^{+} + R_4, \quad (4)$$

$$NpO_2^{2+} + R_4 \rightarrow NpO_2^{+} + \text{products}. \quad (5)$$

As noted in [5], excess carbohydrazide reacts with Np(VI) to form a gas phase containing N_2, CO_2, and a small amount of N_2O. Hence, a certain step of reactions (2)–(5) involves the hydrolysis of the radical with the elimination of N_2H_x and H_2CO_3 groups.

The kinetics of the Np(VI) + $H_n(NH_2NH)_2CO^{n+}$ reaction was studied in 0.1–2.0 M $HClO_4$ solutions at the ionic strength I = 2.0, supported by adding $LiClO_4$. The reaction stoichiometry allowed performing studies at the carbohydrazide concentration exceeding the Np(VI) concentration by a factor of only 3. Figure 1 shows the kinetic curves in the coordinates $\log(D_\infty - D)$–time at T = 30°C. For a 2 M $HClO_4$ solution containing 1 mM Np(VI) and 100 mM carbohydrazide, the kinetic dependence is a straight line up to 95% conversion. In solutions containing 50 and 20 mM carbohydrazide, the reaction noticeably decelerates after 86 and 77% conversion, respectively. We failed to account for this fact.

Linearization of the kinetic curves in the semilog coordinates shows that the reaction is first-order with respect to Np(VI). Therefore, the rate equation can be presented in the form

$$-d[Np(VI)]/dt = k'[Np(VI)] = k'([Np(V)]_\infty - [Np(V)]), \quad (6)$$

where k' is the first-order rate constant. In the integral form, after the replacement of [Np(V)] by the proportional quantity D, Eq. (6) transforms into the expression

$$2.303\log(D_\infty - D) = k't + \text{const}. \quad (7)$$

Here, D and D_∞ are the running and final optical densities, respectively.

The first-order rate constant increases proportionally to the carbohydrazide concentration. The data obtained in a 2 M $HClO_4$ solution containing 1 mM Np(VI) are given in Table 1.

The fact that the bimolecular rate constant $k_1 = k'[(NH_2NH)_2CO]$ is independent of the carbohydrazide concentration shows that the reaction is first-order with respect to the reductant; here, k_1 includes the rate constant of reaction (1) and of the subsequent fast reactions of the radicals with Np(VI). The k_1 values obtained under different conditions are given in Table 2.

As seen from Table 2, the Np(VI) reduction sharply decelerates with increasing H^+ concentration. Figure 2 shows the log–log dependences of k_1 on [H^+]. At 25 and 30°C, the experimental points fall on straight lines with a slope of –1.45. Hence, the reduction occurs via formation of an activated complex with the elimination of one and two protons. The activated complex is

Table 1. Results of kinetic experiments in a 2 M $HClO_4$ solution containing 1 mM Np(VI)

T, °C	$[(NH_2NH)_2CO]$, mM	$k' \times 10^3$, s^{-1}	k_1, L mol^{-1} s^{-1}
25	3	0.157	0.0523
	6	0.32	0.0533
	10	0.51	0.051
	20	1.02	0.051
	40	2.04	0.051
	100	5.97	0.060
30	3	0.312	0.104
	10	1.057	0.106
	20	2.034	0.102
	50	5.5	0.11
	100	9.91	0.099

Table 2. Influence of conditions on the bimolecular rate constant of the Np(VI) + $(NH_2NH)_2CO$ reaction. I = 2 M, [Np(VI)] = 1 mM, $[(NH_2NH)_2CO]$ = 3–100 mM

T, °C	$[HClO_4]$, M	k_1, L mol^{-1} s^{-1}
25	2	0.052
	1	0.12
	0.5	0.54
	0.2	1.76
	0.1	4.06
30	2	0.104
	1	0.345
	0.5	0.857
	0.2	2.79
	0.1	8.03
35	2	0.176
40	2	0.296
45	2	0.495

formed by the reactions

$$NpO_2^{2+} + H(NH_2NH)_2CO^+ \rightleftarrows NpO_2(NH_2NH)_2CO^{2+} + H^+,$$

$$NpO_2^{2+} + H_2(NH_2NH)_2CO^{2+} \rightleftarrows NpO_2(NH_2NH)_2CO^{2+} + 2H^+.$$

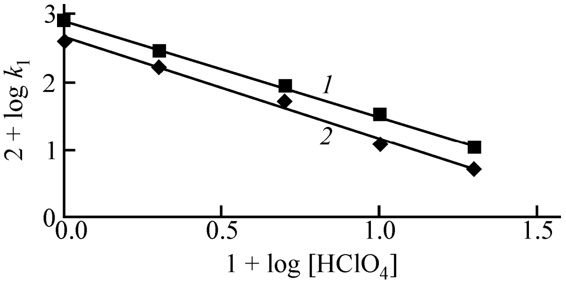

Fig. 2. Influence of the concentration of H^+ ions on the bimolecular rate constant of the Np(VI) reduction with carbohydrazide in a solution with the ionic strength I = 2 M. T, °C: (*1*) 25 and (*2*) 30.

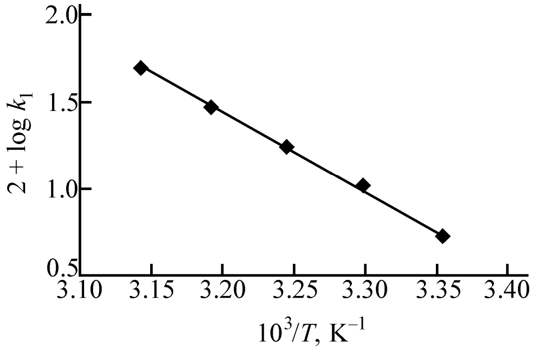

Fig. 3. logk_1 of the Np(VI) reduction with carbohydrazide as a function of reciprocal temperature. $[HClO_4]$ = 2 M and $[(NH_2NH)_2CO]$ = 3 mM.

This is followed by the intramolecular charge transfer with the formation of NpO_2^+ and R.

The rate equation taking into account all the participants of the Np(VI) reduction with carbohydrazide in an $HClO_4 + LiClO_4$ solution can be written in the form

$$-d[Np(VI)]/dt = k'[NpO_2^{2+}][(NH_2NH)_2CO][H^+]^{-1.45},$$

where k = 0.12 $L^{-0.45}$ $mol^{0.45}$ s^{-1} at $[H^+]$ = 1 M and T = 25°C.

From the temperature dependence of k_1 in the coordinates $10^3/T$ (K^{-1})–logk_1 (Fig. 3), we found the activation energy: 86 ± 5 kJ mol^{-1}.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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